

**Thermodynamic Properties of New Refrigerants,
Pentafluoroethyl Methyl Ether and Heptafluoropropyl Methyl Ether¹**

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Abstract

Thermodynamic properties of two fluorinated ethers, that meet the criteria with considerably low global warming potential besides the zero ODP among the promising new-generation refrigerants, are studied in the present study. The recommended candidates are pentafluoroethyl methyl ether, $\text{CF}_3\text{CF}_2\text{OCH}_3$ (245cbE $\beta\gamma$), and heptafluoropropyl methyl ether, $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$ (347sE $\gamma\delta$), proposed as alternative refrigerants to replace 1,2-dichloro-1,1,2,2-tetrafluoroethane, $\text{CClF}_2\text{CClF}_2$ (R-114) and trichlorofluoromethane, CCl_3F (R-11), respectively. The present paper summarizes the current thermodynamic property studies of the above fluorinated ethers, and their thermodynamic property modeling will be presented. The formulations are completed based on the *PVT* property data fitting, both in the single phase and at the saturation states, considering additional thermodynamic behavior of the heat capacities and speeds of sound derived.

KEY WORDS: alternative refrigerants; equation of state; fluorinated ethers; *PVT* properties; thermodynamic properties.

1. Introduction

In the last several years, R&D projects to investigate some potential compounds having lower GWP than HFC, as well as zero ODP, have been established in developed countries. The basic purpose of such new project is anticipating the possible banning of HFCs, which have been expected as promising alternative refrigerants, due to their considerable global warming potential. In addition to the increasing interest in the natural refrigerants to solve the “HFC banning issue”, there exists a challenge to develop environmentally-benign chemical compounds as new-generation refrigerants. The latter is carried out in Japan through a national project to synthesize fluorinated ethers that have thermodynamic properties similar to that of fluorocarbon refrigerants [1].

There are numbers of potential fluorinated ethers studied within the project. The present paper, however, will focus only on pentafluoroethyl methyl ether, $\text{CF}_3\text{CF}_2\text{OCH}_3$ (245cbE $\beta\gamma$), and heptafluoropropyl methyl ether, $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$ (347sE $\gamma\delta$), proposed as promising alternative refrigerants to replace 1,2-dichloro-1,1,2,2-tetrafluoroethane, $\text{CClF}_2\text{CClF}_2$ (R-114) and trichlorofluoromethane, CCl_3F (R-11), respectively. As usually found concerning new chemical compounds, studies on the thermodynamic properties of $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$ are very limited. At the current status, they are limited only to the measurements of vapor pressures, *PVT* properties and critical parameters. The first part of the present paper reviews the available experimental studies of the thermodynamic properties of the fluorinated ethers of the present interest. It is then followed by the formulation of the measured properties through correlations and equations of state developed. A discussion of the developed formulations will conclude the present paper.

2. Experimental Studies on $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$

The reported experimental studies on $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$ have been carried out up to the present only by two laboratories, i.e., Sako et al. [2, 3] at the National Institute of Materials and Chemical Research, Tsukuba, Japan, and our group at Keio University, Yokohama, Japan, through Tsuge et al. [4], Uchimura et al. [5], Ohta et al. [6, 7] and Yoshii et al. [8]. First report by Sako et al. [2] covers the vapor pressure measurements from the normal boiling point to the critical point of some fluorinated ethers including $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$. Vapor pressure correlations were also developed on the basis of their measurements. The second paper [3] dealt with the measurements of critical temperature, critical pressure and critical density of similar fluorinated ethers by direct visual observation method.

Tsuge et al. [4] and Uchimura et al. [5] of our laboratory measured vapor pressures and PVT properties of $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$, respectively, by using an isochoric apparatus. However, the measured PVT property data exist more in gaseous phase than in liquid phase. Ohta et al. [6, 7] challenged the PVT property measurements in liquid phase to complement the earlier works by Tsuge et al. and by Uchimura et al., although for pressures up to 3 MPa. Yoshii et al. [8] completed measurements of the saturation densities along the vapor-liquid coexistence curve near the critical point and determined the critical temperature and critical density of $\text{CF}_3\text{CF}_2\text{OCH}_3$. All the works on the thermodynamic properties of $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$ are summarized in Table 1 along with their measured ranges, experimental uncertainties, and purities of the samples used.

3. Saturation Properties of CF₃CF₂OCH₃ and CF₃CF₂CF₂OCH₃

Measured vapor pressures are correlated in the present study in a functional form given by Eq. (1).

$$T_r \ln P_r = A_1(1-T_r) + A_2(1-T_r)^{1.5} + A_3(1-T_r)^3 + A_4(1-T_r)^6 \quad (1)$$

T_r and P_r in Eq. (1) are defined T/T_C and P/P_C , respectively, with the critical temperature, T_C , and critical pressure, P_C . The T_C value used in the present work was that measured by Yoshii et al. [8] for CF₃CF₂OCH₃ and by Sako et al. [3] for CF₃CF₂CF₂OCH₃, while P_C was determined in the present study based on the available vapor-pressure data. The numerical coefficients in Eq. (1) for CF₃CF₂CF₂OCH₃ are optimized on the basis of the data by Ohta et al. [6] and by Uchimura et al. [5], while those of CF₃CF₂OCH₃ on the basis of the data by Tsuge et al. [4] and Ohta et al. [7]. T_C , P_C , and coefficients $A_1 - A_4$ are given in Table 2. Figures 1(a) and 1(b) depict the absolute deviation of measured vapor pressures of CF₃CF₂OCH₃ and CF₃CF₂CF₂OCH₃ from Eq. (1), showing excellent agreement within ± 2 kPa in both cases.

Based on the saturated-liquid densities measured by Tsuge et al. [4], Ohta et al. [7], and Yoshii et al. [8] for CF₃CF₂OCH₃, by Uchimura et al. [5] and Ohta et al. [6] for CF₃CF₂CF₂OCH₃, a saturated-liquid density correlation, Eq. (2), has been developed.

$$\rho' = \rho_C \left[1 + B(1-T_r)^\beta + \sum_{i=1}^3 B_i(1-T_r)^{b_i/3} \right] \quad (2)$$

ρ' in Eq. (2) denotes the saturated-liquid density. The critical density, ρ_C , used in Eq. (2) for CF₃CF₂OCH₃ is that measured by Yoshii et al. [8], while for CF₃CF₂CF₂OCH₃ by Sako et al. [3]. The critical exponent, β , determined by Yoshii et al. for CF₃CF₂OCH₃ is introduced in Eq. (2). Number of terms in Eq. (2) for CF₃CF₂CF₂OCH₃ was limited only to two due to restricted data availability at higher

temperatures. The critical densities, critical exponents, exponents $b_1 - b_3$, coefficient B , and coefficients $B_1 - B_3$ are also tabulated in Table 2. Figures 2(a) and 2(b) illustrate the saturated-liquid density data deviation of $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$ from Eq. (2), respectively.

4. Equation of States for $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$

Based on the available data summarized above and with the aid of Eqs. (1) and (2), we have developed the modified BWR type equations of state (EOS) for $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$ with a functional form given in Eq. (3).

$$P_r = \frac{\rho_r T_r}{Z_c} + a_1 \rho_r^2 \exp\left(\frac{1}{T_r}\right) + \sum_{i=2}^{13} a_i T_r^{\alpha_i} \rho_r^{\delta_i} + \sum_{i=14}^{17} a_i T_r^{\alpha_i} \rho_r^{\delta_i} \exp(-\rho_r^2) \quad (3)$$

ρ_r in Eq. (3) is the reduced density, $Z_c = P_c/(\rho_c R T_c)$ and $R = R_0/M$, whose numerical values are listed in Table 2. The coefficients $a_1 - a_{15}$, the exponents $\alpha_2 - \alpha_{18}$ and $\delta_2 - \delta_{18}$ are given in Table 3. The exponents $\alpha_2 - \alpha_{18}$ and $\delta_2 - \delta_{18}$ are adopted from those used by Piao et al. [9] for hydrofluorocarbons, while the second term of Eq. (3) is that adopted by Zhang et al. [10] for representing the second virial coefficients of hydrofluorocarbons.

Figure 3(a) and 3(b) show the pressure and density deviations of measured *PVT* properties from Eq. (3) for $\text{CF}_3\text{CF}_2\text{OCH}_3$. The data by Tsuge et al. [4] are represented within ± 1 % in pressure but rather greater within ± 6 % in density. The measured saturated-vapor densities are available only for limited temperatures above 358 K, and this causes difficulties in representing the saturation boundaries. Neglecting the saturation boundaries, we found that fitting Eq. (3) exclusively to the *PVT* properties produced a better representation within ± 0.6 % in pressure and ± 3 % in density. The

data by Ohta et al. [7] that show larger pressure deviation are treated with minor weightings in the optimization process of Eq. (3).

Figure 4(a) and 4(b) show the *PVT* property data representations for $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$. The saturated-vapor densities available at present are only four data points by Uchimura et al. [5] above 370 K, and this fact led, in the present study, to add some predicted values during the EOS optimization. As shown in Figs. 4(a) and 4(b), Eq. (3) reproduced the *PVT* properties by Uchimura et al. [5] within $\pm 0.8\%$ in pressure and $\pm 5.5\%$ in density. In relation with the compressed-liquid densities by Ohta et al. [6], Eq. (3) represents the measured data in excellent agreement within $\pm 0.05\%$.

As discussed in the previous section, no thermodynamic property data other than the essential saturation properties and single phase *PVT* properties are available up to the present time for these new fluorinated ethers, and moreover the available *PVT* properties are reported for a limited range of temperatures, pressures and densities. Such a situation has led, firstly, to limiting number of terms for EOS in the present study as given in Table 3. Secondly, examination of the thermodynamic behavior of the derived properties, such as the heat capacities, speeds of sound and the Joule-Thompson coefficients, can only be done qualitatively as given in Figs. 5(a) and 5(b) where the typical examples for the isobaric heat capacities, C_p are illustrated for both compounds. The isobaric heat capacities at ideal gas condition, C_p^0 , for the present calculation were predicted by using the model proposed by Rihani-Doraismamy [11] that resulted in Eq. (4), whose coefficients are tabulated in Table 4.

$$\frac{C_p^0}{R} = c_1 + c_2 T + c_3 T^2 + c_4 T^3 \quad (4)$$

Figures 5(a) and 5(b) depict C_p values of $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$

derived from Eq. (3) that demonstrate the typical physically-sound behavior of pure fluid, at least at the reduced temperature T_r range displayed. Below $T_r = 0.7$, C_p in the liquid phase increases with decreasing temperature. Similar behavior is observed in relation with isochoric heat capacities, C_v , of both compounds. The calculated speeds of sound, as demonstrated in Figs. 6(a) and 6(b), also show the typical sound behavior of pure fluid, except for liquid phase of $\text{CF}_3\text{CF}_2\text{OCH}_3$ at temperatures about $T_r < 0.8$, where the value tends to become slightly smaller. All these fact can be considered to reflect the limited number of terms used in Eq. (3), and the absence of heat capacity data for fluorinated ethers to be used in EOS optimization. For the practical purpose, however, it is believed that Eq. (3) does work more satisfactorily with a thermodynamic consistency than any conventional generalized models.

5. Conclusion

The thermodynamic properties of pentafluoroethyl methyl ether, $\text{CF}_3\text{CF}_2\text{OCH}_3$ (245cbE $\beta\gamma$), and heptafluoropropyl methyl ether, $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$ (347sE $\gamma\delta$), available up to the present have been reviewed and correlated in the present study. The modified BWR type equation of state, which represents satisfactorily the available measured data and shows properly the derived thermodynamic properties, have also been developed.

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Table 1

Reported Measurements Concerning $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$

Substance	First Author	Properties	Range	Uncertainty	Sample Purity
$\text{CF}_3\text{CF}_2\text{OCH}_3$	Sako (1994)	P_s	300 K – T_C up to P_C	± 50 mK ± 2 kPa	99.9 mass%
	Sako (1996)	T_C P_C ρ_C	406.8 K 2.887 MPa 499 kg·m ³	± 30 mK ± 2 kPa ± 0.2 %	99.9 mass%
	Tsuge (1998)	P_s PVT	310 K – T_C up to 8.4 MPa 75 – 854 kg·m ³	± 1 mK ± 1.4 kPa ± 0.07 %	99.9967 mass%
	Ohta (1999)	P_s ρ PVT	260 – 370 K up to 3 MPa 1000 – 1250 kg·m ³	± 8 mK ± 2 kPa ± 2.2 kg/m ³	99.9 mass%
	Yoshii (2000)	T_C P_C ρ_C	406.83 K 2.887.3 MPa 509 kg·m ³	± 17 mK ± 1.5 kPa ± 3 kg/m ³	99.9967 mass%
$\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$	Sako (1994)	P_s	300 K – T_C up to P_C	± 50 mK ± 2 kPa	99.5 mass%
	Sako (1996)	T_C P_C ρ_C	437.7 K 2.481 MPa 530 kg·m ³	± 30 mK ± 2 kPa ± 0.2 %	99.5 mass%
	Uchimura (1998)	P_s PVT	340 – 450 K up to 5.6 MPa 54 – 896 kg·m ³	± 10 mK ± 1.0 kPa ± 0.2 %	99.4 mass%
	Ohta (1998)	P_s ρ PVT	250 – 370 K up to 3 MPa 1100 – 1600 kg·m ³	± 8 mK ± 2 kPa ± 0.2 %	

Table 2

Coefficients in Eqs. (1) and (2) for $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$

	$\text{CF}_3\text{CF}_2\text{OCH}_3$	$\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$
T_c / K	406.83	437.7
P_c / MPa	2887	2476
$\rho_c / \text{kg}\cdot\text{m}^{-3}$	509	530
$M / \text{kg}\cdot\text{kmol}^{-1}$	150.054	200.067
A_1	-7.73986	-7.95132
A_2	1.52151	1.50989
A_3	-4.05631	-4.48124
A_4	-11.0921	-20.8350
β	0.324	0.325
b_1	2	2.36
b_2	4	-
b_3	6	-
B	1.43926	1.81014
B_1	1.69075	0.98763
B_2	-1.54018	-
B_3	1.57395	-

Table 3

Coefficients in Eq. (3) for $\text{CF}_3\text{CF}_2\text{OCH}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$

i	$\text{CF}_3\text{CF}_2\text{OCH}_3$			$\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$		
	a_i	α_i	δ_i	a_i	α_i	δ_i
1	-2.30459069			-2.13053221		
2	4.575640345	0	2	4.737139572	0	2
3	-3.548871317	-1	2	-4.34257279	-1	2
4	3.38002293	1	3	2.735375495	1	3
5	-7.194872802	0	3	-5.09301159	0	3
6	4.847605655	-2	3	7.333999069	-2	3
7	6.463810355	0	4	3.984526051	0	4
8	-0.552837053	-2	4	-1.90229101	-2	4
9	-5.147172957	0	5	-3.47980776	0	5
10	-1.373221473	-1	5	-2.41464629	-1	5
11	2.2724505	0	6	2.142586448	0	6
12	0.230355795	-1	6	0.756726027	-1	6
13	-0.285737347	0	7	-0.40062628	0	7
14	-0.646069613	0	3	2.234616913	0	3
15	0	-1	3	-4.95489876	-1	3
16	-4.750435429	0	5	-3.80397906	0	5
17	4.371599416	-1	5	3.371400347	-1	5

Table 4

Coefficients in Eq. (4)

	$\text{CF}_3\text{CF}_2\text{OCH}_3$	$\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$
c_1	-0.5114	-1.9984
c_2	6.4291×10^{-2}	9.0166×10^{-2}
c_3	-4.7052×10^{-5}	-6.9286×10^{-5}
c_4	1.6976×10^{-8}	1.8152×10^{-8}

FIGURE CAPTIONS

Fig. 1. Vapor pressure deviation from Eq. (1): (a) for $\text{CF}_3\text{CF}_2\text{OCH}_3$, (b) for $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$

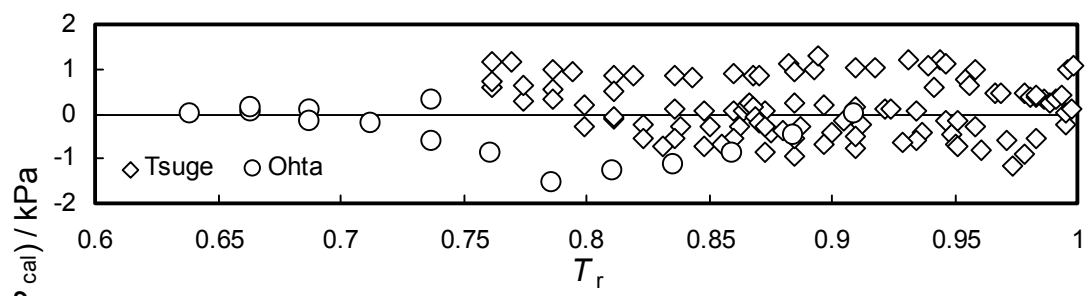
Fig. 2. Saturated-liquid density deviation from Eq. (2): (a) for $\text{CF}_3\text{CF}_2\text{OCH}_3$, (b) for $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$

Fig. 3. *PVT* property deviation from Eq. (3) for $\text{CF}_3\text{CF}_2\text{OCH}_3$: (a) in pressure (b) in density

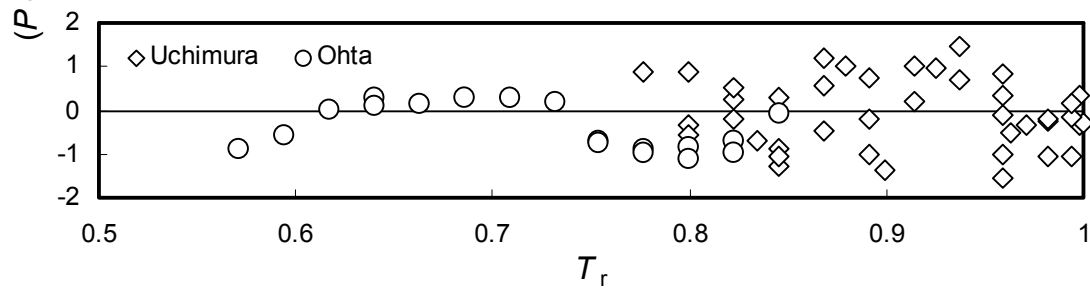
Fig. 4. *PVT* property deviation from Eq. (3) for $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$: (a) in pressure (b) in density

Fig. 5. Isobaric Heat Capacities derived from Eq. (3): (a) for $\text{CF}_3\text{CF}_2\text{OCH}_3$, (b) for $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$

Fig. 6. Speeds of Sound derived from Eq. (3): (a) for $\text{CF}_3\text{CF}_2\text{OCH}_3$, (b) for $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$

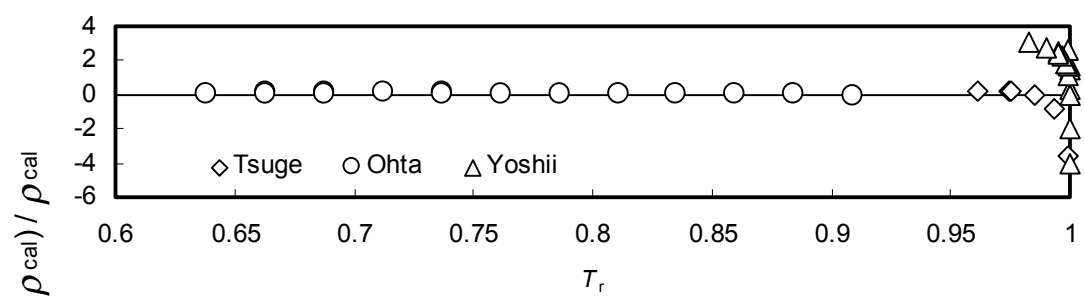


(a)

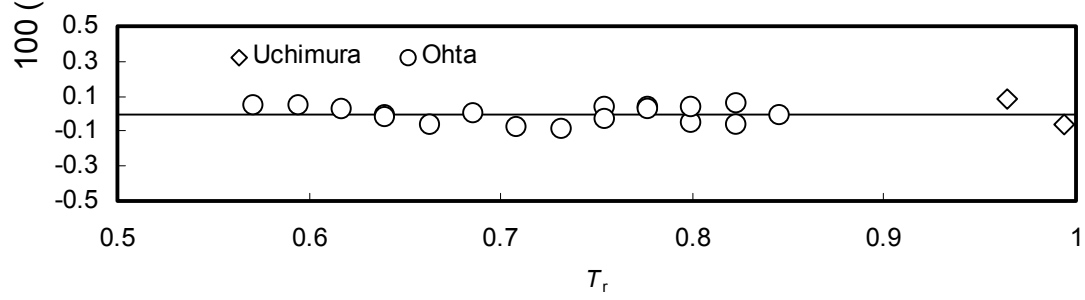


(b)

Fig. 1



(a)



(b)

Fig. 2

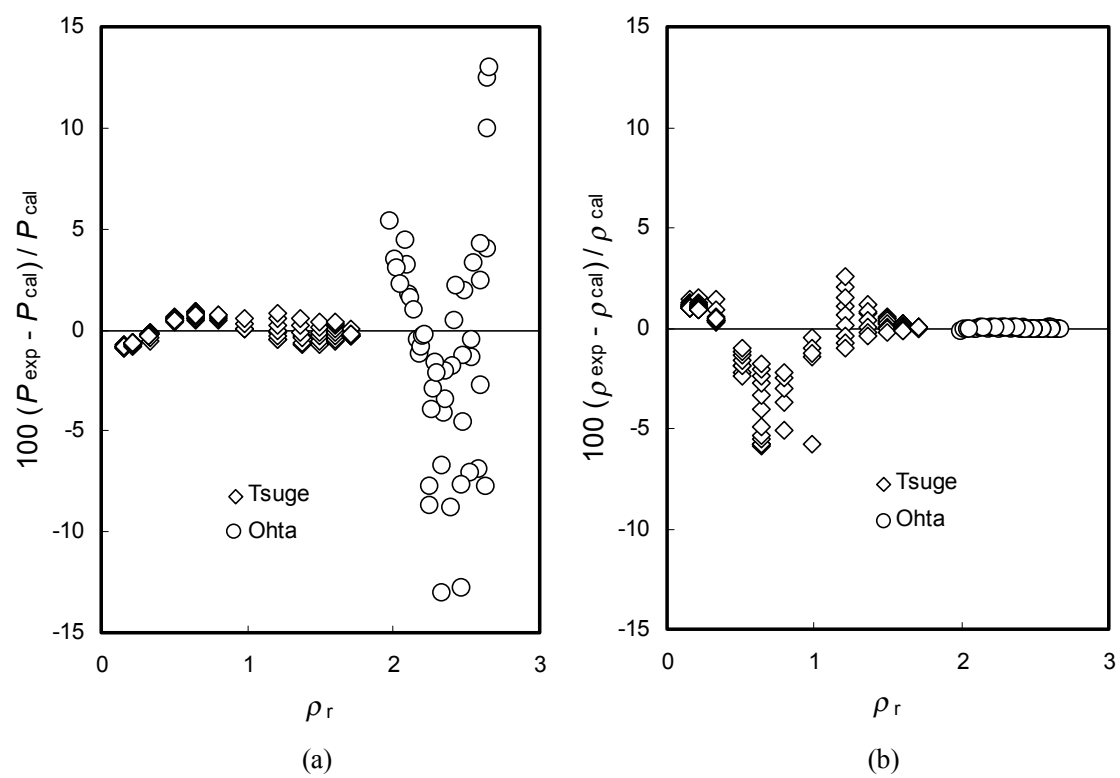


Fig. 3

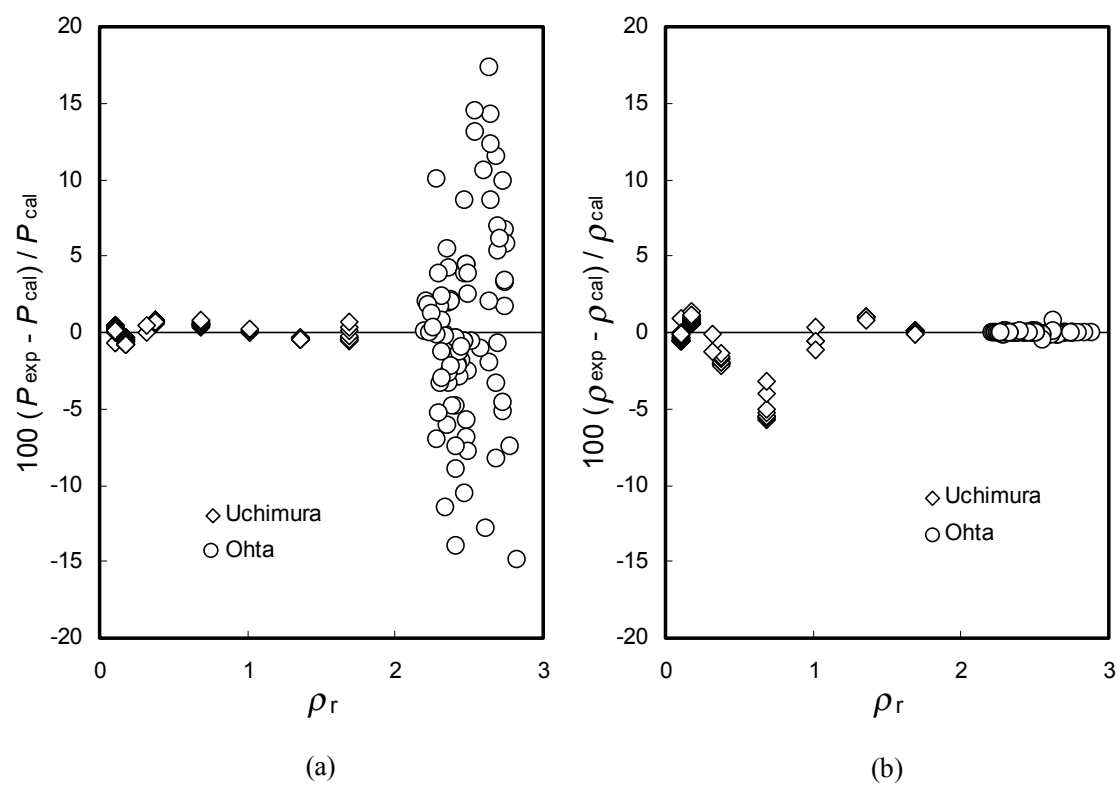
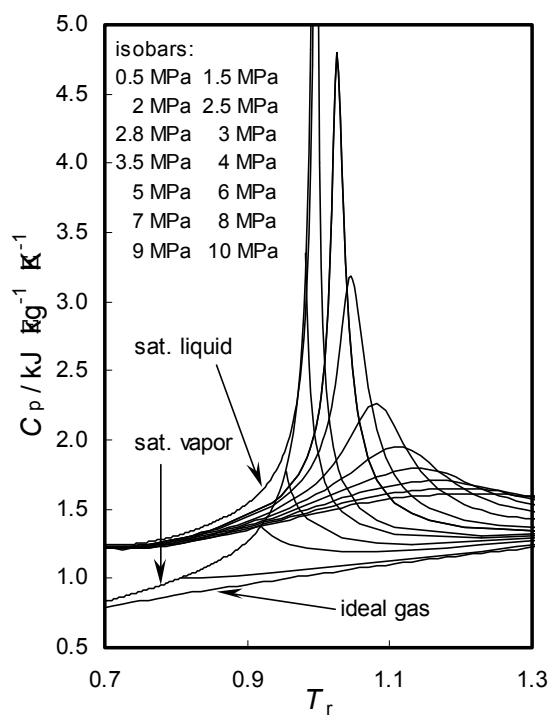
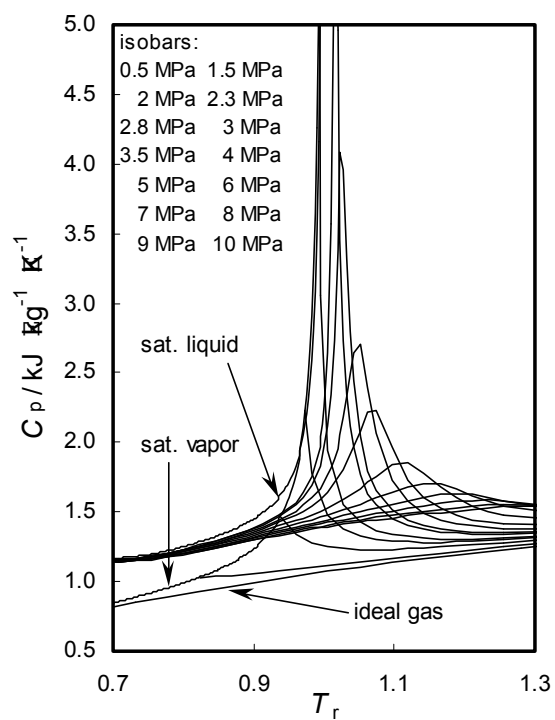


Fig. 4

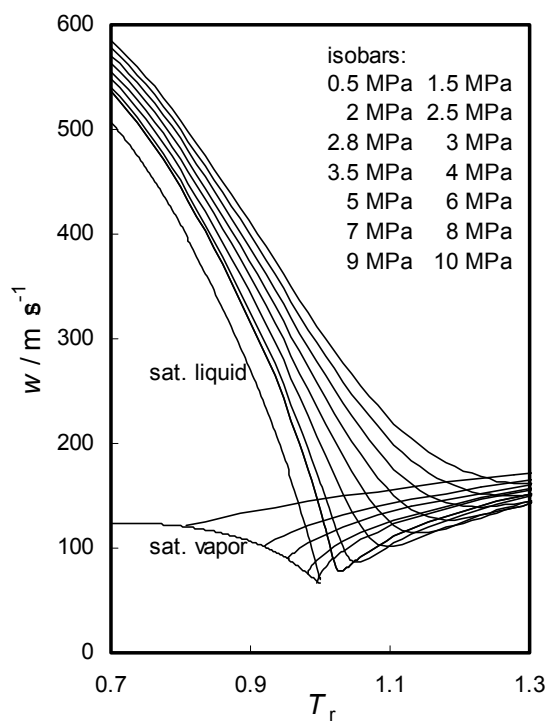


(a)

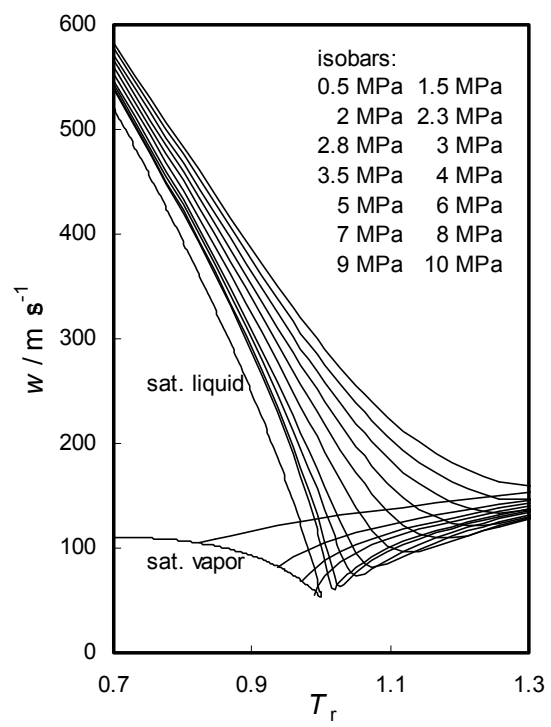


(b)

Fig. 5



(a)



(b)

Fig. 6